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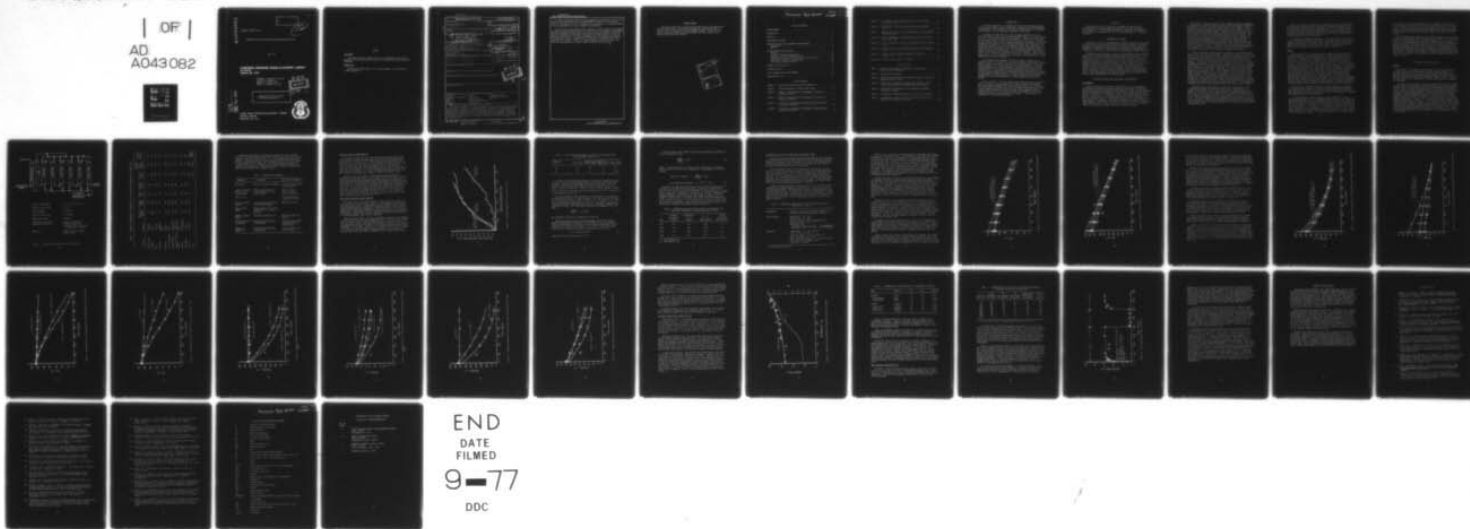
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EVALUATION OF AN AIR STRIPPING-OZONE CONTACTOR SYSTEM.(U)  
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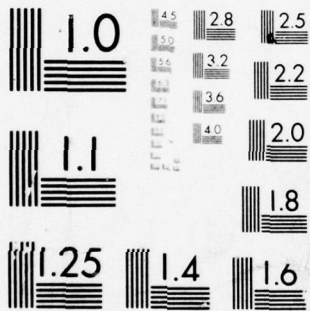
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TECHNICAL REPORT 7707

EVALUATION OF AN AIR STRIPPING-OZONE CONTACTOR SYSTEM

JUNE 1977

**US ARMY MEDICAL BIOENGINEERING RESEARCH and DEVELOPMENT LABORATORY**  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The latest generation of modular shelter, power, and health care equipment for Army field hospitals is termed the MUST: Medical Unit, Self-Contained, Transportable. Supporting the MUST-equipped hospital is a Water Processing Element (WPE) designed to treat non-sanitary hospital wastewater for reuse. Treatment train processes of the WPE are hydraulic equalization, ultrafiltration, reverse osmosis (RO), ultraviolet (UV) activated ozone oxidation, and hypochlorination.		

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A nominal one-quarter scale UV-ozone contactor was evaluated at the US Army Medical Bioengineering Research and Development Laboratory. The contactor, built by Life Systems, Inc., of Cleveland, OH, consisted of six sparged columns in series preceded by an ozone scrubber or precontactor.

The contactor was evaluated using a synthetic clinical hospital RO permeate. Evaluation included defining the fluid regime inside the columns, investigating the effectiveness of pre-stripping, and monitoring the oxidation of selected laboratory wastewater components throughout the oxidation process as well as measuring TOC and COD. A correlation between the TOC stripping rate constant and oxygen mass transfer coefficient was developed in cooperation with the University of Illinois. Effects of ozone concentration and UV light on the kinetics and mechanisms of organic carbon oxidation were explored.

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## INTRODUCTION

The latest generation of equipment for Army field hospitals derives from a building-block concept called MUST: Medical Unit, Self-Contained, Transportable. MUST-equipped field hospitals are designed to be highly mobile centers of care deployable anywhere in the world.

To enhance the mobility of the MUST-equipped hospitals in water deficient areas, a MUST Water Processing Element (WPE) is being developed for reuse of nonsanitary hospital wastewaters. The MUST WPE will have a nominal product water capacity of 3500 gallons per day (gpd). Operating in one configuration, it will renovate nonsanitary wastewater to a quality acceptable for nonpotable and eventually potable reuse. Operating in a second configuration, it will simultaneously treat those same waters for discharge to the environment while treating fresh or brackish natural waters for potable and other uses. Six nonsanitary wastewaters have been characterized from a MUST-equipped mobile field hospital. These wastewaters are of industrial rather than municipal or domestic nature. Wastewater sources include operating room, kitchen, X-ray laboratory, clinical laboratory, shower, and laundry.<sup>1</sup>

The candidate unit processes for the WPE reuse operation are, in sequence: hydraulic equalization, 40-mesh screening, ultrafiltration (UF), reverse osmosis (RO), ozone oxidation with ultraviolet (UV) light, and hypochlorination. Of the several unit processes proposed for the WPE reuse treatment train, ozone oxidation is the least optimized and most controversial.<sup>2</sup> Pilot studies and full-scale applications have demonstrated a certain potential for ozone oxidation or disinfection in domestic wastewater treatment plants.<sup>3</sup> Industrial applications for phenol and cyanide reductions are operational.<sup>4</sup> Ozone oxidation of nonsanitary wastewaters of the type expected from MUST-equipped Army hospitals is unique.

Initial efforts in the Army ozone program were presented by Reuter in 1973.<sup>5</sup> By that time the feasibility of ozone oxidation of selected MUST-type organic compounds was shown, and the necessity for incorporation of ultraviolet light to aid in their removal was established. Subsequent efforts ranged from detailed bench scale parametric testing through fabrication of pilot scale equipment and detailed analysis of automatic control and instrumentation procedures. These efforts are referenced in the following sections.

## OBJECTIVE

The objective of this study was to evaluate a pilot scale air stripping-ozone contactor system designed and built for the Army by Life Systems, Inc. of Cleveland, Ohio and to investigate the effects of pre-stripping on subsequent ultraviolet aided ozonation of a selected wastewater.

## EXPERIMENTAL APPROACH

Evaluation of the air stripper-ozone contactor consisted of measuring its hydraulic mixing, physical stripping, chemical oxidation, and mass transfer characteristics under controlled conditions using a specified wastewater. Treatability studies were also made on the wastewater to investigate the effect of pre-stripping on subsequent UV-aided ozonation.

Treatability was measured in terms of the wastewater's total organic carbon (TOC) removal and chemical oxygen demand (COD) reduction. For these cases a reliable TOC/COD trend over time was desired for each pre-stripping situation. COD and TOC results were plotted to determine whether additional runs should consist of reruns to better define the trend for specified pre-stripping times or should consist of other intermediate pre-stripping times to further define the differences among trends. Scatter of the data did not readily indicate smooth trends. Reruns were made to insure that the standard error of estimate for the line of regression (trend) through the data was kept to an acceptable value. Runs which measured TOC and COD reduction were repeated either once or twice depending on the resulting data.

## CONTRACTOR DESIGN AND DEVELOPMENT CONSIDERATIONS

### DEVELOPMENT

During the period of time when Life Systems, Inc. (LSI) designed, developed, and tested their ozone contactor, significant information about the kinetics and mechanism of the ozonation process on MUST-equipped hospital wastewaters was gathered in bench scale studies done by Chian,<sup>6</sup> Sierka,<sup>7</sup> and Zeff,<sup>8</sup> and in bench and pilot scale studies done by Gollan et al.<sup>9</sup> Furthermore, a significant paper had been published by Hill<sup>10</sup> in which he measured the liquid phase ozone mass transfer coefficients in a gas sparged ozone reactor. Additional important work had been done by Hewes et al.,<sup>11</sup> investigating oxidation of refractory organic materials by ozone and ultraviolet light. The term "refractory" used in this report refers to materials relatively resistant to ozone oxidation.

Work done by the investigators on MUST-equipped hospital wastewaters was performed in different reactors under varying experimental conditions. Nevertheless, several conclusions were common to all studies: There existed an initial period of relatively high rate TOC removal in which values of dissolved ozone measured in aqueous solution were very low. This indicated mass transfer played a major role in the reaction. After the initial, relatively high TOC removal period, the TOC removal rate declined significantly indicating the presence of ozone resistant or ozone refractory compounds in solution, especially when ozonating MUST clinical laboratory wastewater. This slower TOC removal rate was accompanied by a significant and relatively stable dissolved ozone content and was felt to be principally reaction rate limited, or at least "not mass transfer limited."<sup>7</sup> Finally, it was observed that ultraviolet light together with ozone increased the rate of oxidation and rate of subsequent TOC removal of the refractory compounds in solution.

Other miscellaneous findings were also noted by these investigators upon ozonating MUST-type wastewaters. Sierka<sup>7</sup> found greater rates of TOC removal at alkaline pH values. This observation was repeated by the other investigators and supported theories put forth by Hewes<sup>12</sup> and Stumm<sup>13</sup> regarding the role of the hydroxyl ion during ozone decomposition and reaction. Drawing on previous experience with stripping volatile organic compounds from aqueous solution, Chian<sup>6</sup> showed TOC removal was a combination of physical stripping and chemical oxidation by ozone which depended upon the quantities of volatile compounds in the mixture being treated and upon the rate of gas flow. Gollan *et al.*,<sup>9</sup> noted an effect of temperature on TOC removal rate. In the range of 30° to 80°C, the rate of removal peaked between 45° and 60°C for most but not all hospital wastewaters studied. X-ray laboratory wastewater was the exception. This variation of the TOC removal rate was felt to be the combination of an increase in the oxidation reaction rate with temperature and a simultaneous decrease in ozone solubility. Gollan also observed that as gas concentration decreased below 2 percent weight ozone in air, TOC removal was limited primarily by mass transfer and that the removal rate declined.

Integrated system ozonation test results by Gollan *et al.*,<sup>9</sup> were disappointing because of equipment malfunctions. Failures in the reactor and generator did not allow ozonation treatment potential to be realized. The "integrated" system referred to simultaneous operation of all MUST Water Processing Element unit processes on a pilot (1000 gpd) scale. Gollan recommended further investigation and evaluation of a 1/8 to 1/4 scale ozone contactor with performance characteristics superior to the one examined. Sufficient liquid phase residence time and high conversion of ozone across the reactor were felt to be important considerations to contactor design.



During its internal research and development activities, LSI reviewed the literature concerning the use of ozone for treating wastewater and reviewed various ozone injection techniques and contact chamber designs.<sup>14</sup> The Torricelli ozone contacting system was felt to have desirable characteristics because it allowed routing of off-gases into a pre-contactor for additional ozone conversion and operated at slightly pressurized conditions beneficial for mass transfer.<sup>15</sup>

LSI adapted the Torricelli concept in a nominal quarter scale contactor which met pragmatic height, power, and volume design considerations imposed by the Army.<sup>16</sup> Provisions were incorporated to allow automatic heating and pH monitoring of the process water. Ultraviolet lights and provisions for manual pH adjustment were also incorporated.<sup>17,18</sup>

### DESIGN

For reactions whose rate increases with reactant concentration, the mixed flow reactor (also termed the backmix reactor or the completely stirred tank reactor, CSTR) always needs a larger volume than the plug flow type.<sup>19</sup> Evaluation of a number of equal sized mixed reactors in series will show that as the number of mixed flow reactors approaches infinity, mixed flow performance approaches that for a single plug flow reactor. Citing efforts by Chian,<sup>6</sup> Sierka,<sup>7</sup> and especially Gollan et al.,<sup>9</sup> LSI noted that the organics in MUST-type hospital wastewaters (especially laboratory wastewaters) were composed of an easily oxidizable portion and of a refractory portion which were largely mass transfer and reaction rate controlled, respectively. Once easily oxidizable organics were removed by ozone oxidation, the refractory portion remained reaction rate controlled and a function of remaining TOC. A six stage, mixed reactor plus precontactor design was chosen. Assuming a first order reaction rate with respect to TOC concentration for the refractory wastewater portion, backmix reactor volume was expected to be 1.3 times that for a plug flow reactor when treating a typical composite hospital wastewater.<sup>20</sup>

Focusing their attention on ways to transfer ozone into solution, LSI noted that any contactor system which could minimize power expenditure for transfer of ozone into aqueous solution was most desirable.<sup>21</sup> Elimination of stirring would be a step in the right direction if adequate mass transfer rates could be attained.

In a program which studied the mass transfer behavior of a gas sparged ozone reactor, Hill<sup>10</sup> showed how rate of reaction, gas flow rate, and bubble diameter affect mass transfer of ozone into bulk solution. As part of his work, Hill calculated liquid phase mass transfer coefficients using the Hughmark correlation for several bubble sizes and gas flows in a sparged column full of tapwater. He reported the Hughmark correlation to be reasonably accurate compared to actual experimental values in cases where reaction took place in the liquid bulk rather than in the laminar film surrounding the bubbles. For a gas flow of 4.5 l/min, bubble size

of 0.10 inch, and an ozone concentration of 3 percent by weight, the liquid phase ozone transfer flux ( $k_x$ ) was calculated to be 7.75 lb-mole/hr-ft<sup>2</sup>. Assuming these conditions and a bubble rise velocity of 0.96 ft/sec, LSI calculated that nearly 90 percent of the equilibrium amount of ozone would be absorbed into aqueous solution in 6 feet of liquid height.<sup>22</sup>

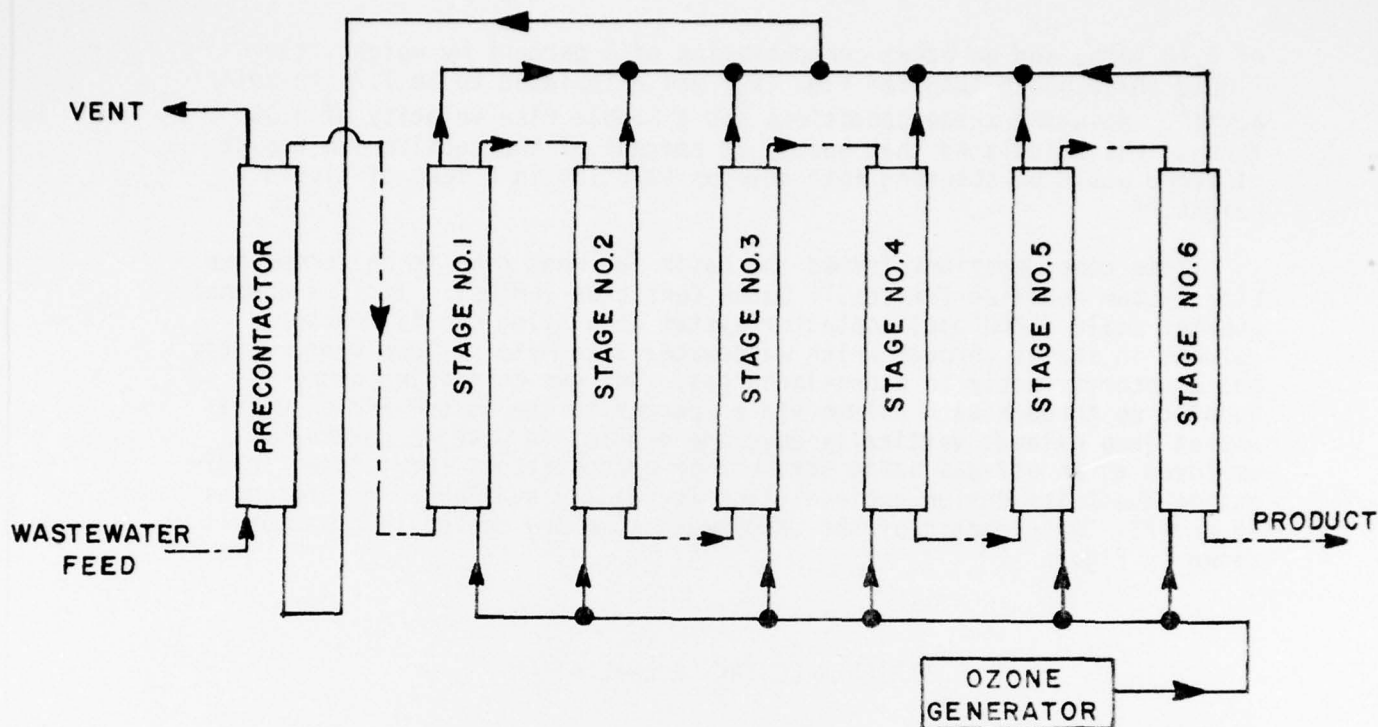
These considerations formed the basis for what came to be termed the Life System Modified Torricelli Ozone Contactor (LMTOC). It is a nominal quarter scale (1000 gpd) contactor system consisting of six reactor columns in series through which wastewater alternately flows concurrently and countercurrently to ozone-laden gas. The gas containing ozone is bubbled up through each column via a sparger in the bottom and an ultra-violet lamp extends vertically down the middle. A seventh column is employed as an off-gas ozone scrubber or precontactor. Additional information about its design and evolution is readily available in references 17 and 23. A schematic of the LMTOC with some key design information is shown in Figure 1.

## STRIPPER-CONTACTOR EVALUATION

### GENERAL

Evaluation of the LMTOC by Life Systems, Inc. had centered mostly on ozone oxidation of MUST-equipped hospital composite waste.<sup>23</sup> It was felt that contactor evaluation and additional experimental work should be done using laboratory wastewater because it contained the most refractory organics and required the longest reaction time.<sup>24</sup> Treatability studies on the LMTOC using laboratory wastewater are presented in this paper.

The basis for the synthetic laboratory wastewater came from a water quality study which evaluated actual MUST-equipped hospital wastewaters in the field.<sup>25</sup> Concentrations of laboratory wastewater constituents found in the field study were modified to take into account ultrafiltration and reverse osmosis treatment laboratory wastewater received before ozonation. Major considerations were the molecular weight and water solubility of the compounds and DuPont B-10 reverse osmosis membrane separation characteristics as measured by Fang and Chian<sup>26</sup> for several organic compounds. A formula for the resulting synthetic laboratory RO permeate used appears in Table 1.<sup>27</sup> The theoretical total organic carbon chemical oxygen demand, and COD/TOC values are also listed. Three relatively volatile compounds, namely methanol (boiling point 64.7°C), acetone (boiling point 56.2°C), and diethyl ether (boiling point 34.6°C), contributed a combined TOC which was 94 percent of the total TOC. Hence, this wastewater appeared to be treatable by gas stripping before or during ozonation.



Overall size (HXWxD):	7.5 ft x 9.3 ft x 4 ft
Volume of each stage:	1.2 ft <sup>3</sup>
Stage diameter :	6.6 inches
Sparger surface area:	14.8 inches
Sparger pore size:	5 microns
Ultraviolet lamp output: (operated at 425 ma)	70 watts total power 34 watts at 253.7 nm 210 $\mu$ watts/cm <sup>2</sup> at 253.7 nm and one meter in dry air
Materials:	stainless steel, teflon, quartz, glass

Figure 1. LMTOC Design Characteristics and Materials.

TABLE 1. SYNTHETIC LABORATORY RO PERMEATE WITH SOME GENERAL CHARACTERISTIC PARAMETERS<sup>27</sup>

Chemical	Formula	Conc. in RO Permeate (mg/l)	Formula Weight (gmw)	Formula TOC (gmw)	Theoreti- cal COD (gmw)	TOC in RO Permeate (mg/l)	Theoreti- cal COD in RO Permeate (mg/l)	Theoreti- cal COD/TOC
Diethyl ether	$(C_2H_5)_2O$	1.8	74.0	48	192	1.2	4.7	4.0
Methanol	$CH_3OH$	289.1	32.0	12	48	108.4	433.7	4.0
Urea	$(NH_2)_2CO$	0.9	60.0	12	48	0.2	0.7	4.0
Glycerol	$(CH_2OH)_2-CHOH$	2.1	92.0	36	112	0.8	2.6	3.1
Ethanol	$C_2H_5OH$	3.3	46.0	24	96	1.7	6.9	4.0
10% Formaldehyde	$HCHO$	10.6	30.0	12	32	4.2	11.3	2.7
<i>o</i> -phenylphenol	$C_6H_5C_6H_4OH$	0.4	170.0	144	448	0.3	1.1	3.1
<i>o</i> -benzyl- <i>p</i> -chloro-phenol	$C_6H_5CH_2C_6H_3ClO$	0.3	218.5	156	488	0.2	0.7	3.1
Xylenol	$(CH_3)_2C_6H_3OH$	0.2	122.0	96	320	0.2	0.5	3.3
Isopropanol	$C_3H_7OH$	0.1	60.0	36	144	0.1	0.2	4.0
Acetone	$(CH_3)_2CO$	32.8	58.0	36	128	20.4	72.4	3.6
TOTAL						137.7	534.8	average 3.88



Laboratory RO permeate stripping was conducted in batch (airflow only) or continuous mode (air and water flow) and took place in the pre-contacter stage of the LMTOC (Fig. 1). It was found most expedient to ozonate in the batch mode since for constant density liquids an element of fluid reacts for the same time in a batch and plug flow reactor.<sup>19</sup> Ozonation took place in stage No. 1 and, unless otherwise noted, the ultraviolet light was on. Procedures, chemical analyses, and equipment used in the evaluation are listed in Table 2.

TABLE 2. PROCEDURES AND ANALYSES

Parameter	Equipment	Materials or Methods
Dye tracer	Model 110 Turner Fluorometer	Uranine (disodium salt of fluorescein)
Oxygen in aqueous solution and oxygen uptake	Yellow Springs Model 54 Oxygen Meter with strip chart recorder	Sodium sulfite cobalt chloride (for deoxygenation)
Ozone in air	-	Standard Methods <sup>28</sup> (Iodometric Method)
Ozone in aqueous solution	Bausch and Lomb Spectronic 700 spectrophotometer	Method of Shector <sup>29</sup>
Total Organic Carbon	Beckman Model 915 or Phase Separation, Ltd. TOCSIN Analyzer	-
Chemical Oxygen Demand	Technicon Autoanalyzer II	Method of Jirka and Carter <sup>30</sup>
Diethyl ether and isopropanol	Hewlett-Packard 5830 Gas Chromatograph	Head space gas chromatography method of Cowen <i>et al.</i> <sup>31</sup>
Acetone and methanol	Hewlett-Packard 5830 Gas Chromatograph	Direct injection gas chromatography

#### HYDRAULIC REGIME CHARACTERISTICS

To begin to characterize the flow regime inside the column, longitudinal dispersion dye runs were made for various gas flows and a water flow rate of 11 gallons per hour (gph) to give 50 minutes theoretical detention time in each column. LSI had sparged its reactors at the rate of 10 standard cubic feet per hour (SCFH) into each 1.2 cubic foot column.<sup>23</sup> Based on their earlier procedures, 10, 20, and 30 SCFH gas flow rates were selected. To relate these gas flow rates to column size, experimental conditions were listed by gas/liquid ratios defined as volume of gas per minute per unit volume of liquid (VVM) after Chian.<sup>6</sup>

Figure 2 shows the behavior of the output dye concentration in response to a step dye input.<sup>32</sup> Gas flows of 10 SCFH (0.13 VVM) indicate an intermediate amount of dispersion whereas those of 20 and 30 SCFH (0.26 and 0.40 VVM, respectively) show a large amount of dispersion which approached that characteristic of washout from vessels under complete mix conditions.<sup>33</sup> The dye response indicated that wastewater in previous tests at 10 SCFH had been less than completely mixed. Furthermore, the dye tests indicated that increasing gas flow above 20 SCFH per column offered no additional advantage in hydraulic mixing. As a result of these tests, 20 SCFH of gas was used when evaluating laboratory RO permeate treatability with ozone on the LMTOC.

#### WASTEWATER STRIPPING CHARACTERISTICS

The significantly different hydraulic regimes due to the higher gas flow rates and the volatile constituents in the wastewater underscored the necessity to further investigate stripping effects. Chian<sup>6</sup> had previously demonstrated the effects of stripping on MUST-equipped hospital composite and laboratory wastewaters, but at high VVM's ( $\geq 1.0$ ) and on a bench scale. Furthermore, Sierka<sup>34</sup> had earlier pointed out the necessity for gathering data on the effect of gas/liquid ratios and the stripping of volatile compounds that could be expected.

Efforts began by batch stripping the synthetic laboratory RO permeate at 28°C and 50°C and VVM values ranging from 0.3 to 0.9.<sup>32</sup> Table 3 shows that TOC removal after 1 hour at 28°C was very poor no matter what the gas flow rate (liquid volume remained constant). Essentially no volatile compounds were stripped. Stripping at 50°C showed some improvement after 60 minutes, rising from 4 percent to 11 percent as the gas flow increased. This latter percentage probably represented most of the acetone and diethyl ether which are the most readily volatile organic constituents.

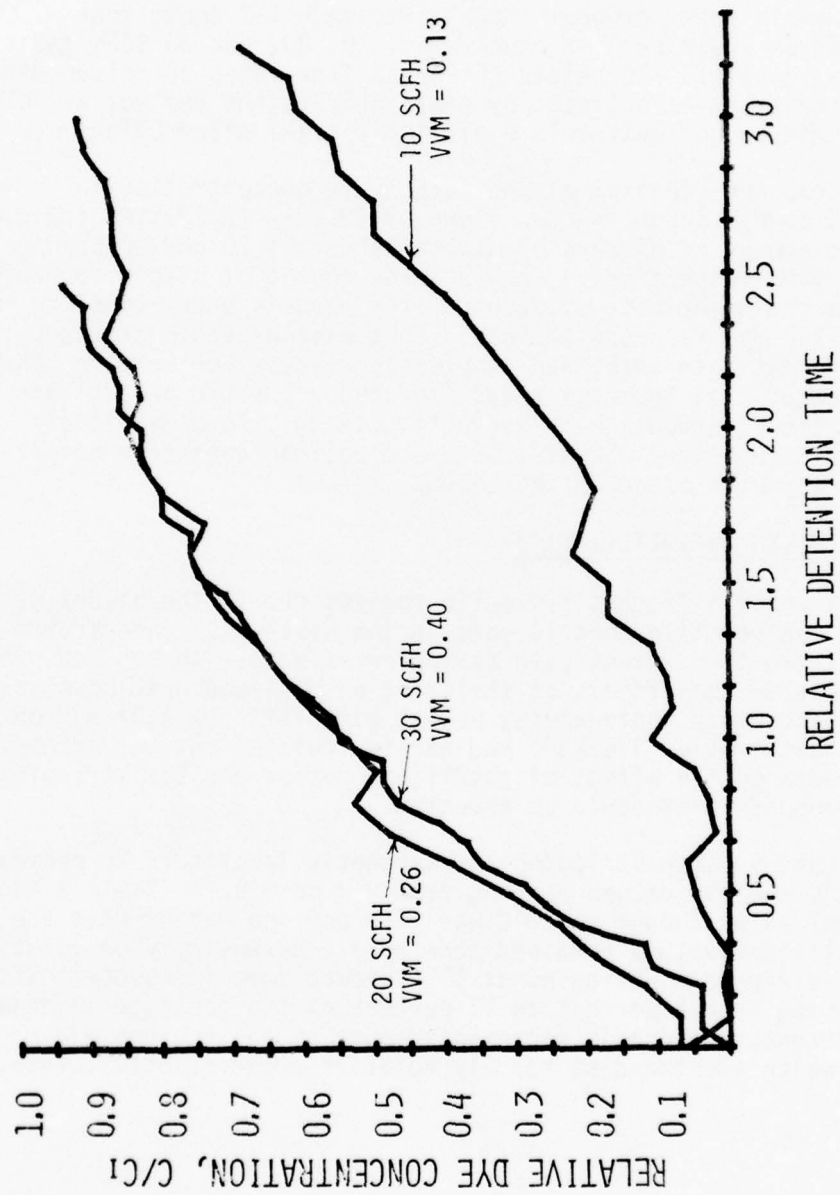


Figure 2. Effluent Response to a Step Tracer Input.

TABLE 3. BATCH STRIPPING SHOWING THE EFFECT OF GAS/LIQUID RATIO AND TEMPERATURE AFTER 1 HOUR

Temperature (°C)	Percent TOC Remaining at			
	VVM = 0.29	VVM = 0.48	VVM = 0.67	VVM = 0.88
28	100	99	97	99
50	97	93	90	88.5

In order to characterize stripping in the LMTOC at various gas/liquid ratios, a common relation between degree of mixing and TOC removal was desirable. Dissolved oxygen uptake measurements were made in an LMTOC chamber filled with tap water employing identical gas/liquid ratios earlier used for stripping.<sup>35</sup> From this data the overall oxygen transfer coefficients,  $k_L a$ , were calculated and averaged 138 to 260  $\text{hr}^{-1}$  across the column depending on the VVM.

Similar procedures were conducted at the University of Illinois by Dr. Edward Chian using a 4 liter fermentor. Air flow rates and agitation intensities were varied in order to obtain a similar range of  $k_L a$ . These latter measurements ranged from 27 to 256  $\text{hr}^{-1}$ . Following this, exactly the same conditions were repeated to strip the laboratory wastewater for a period of 1 hour. The first order stripping rate constant  $k_1$ , of the form

$$\frac{d(\text{TOC})}{dt} = k_1 [\text{TOC}] \quad (1)$$

was determined from TOC data obtained for each run.

Based on stripping and aeration experiments done at the US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) and at the University of Illinois, a linear relation was shown to exist between the stripping rate constant,  $k_1$  at 50°C for laboratory wastewater and the corresponding oxygen transfer coefficient,  $k_L a$ :<sup>36</sup>

$$k_1 = 0.00416 (k_L a)^{0.6} \quad (2)$$

where both  $k_1$  and  $k_L a$  have units in  $\text{hr}^{-1}$ .



Since the rate of TOC removal varies with concentration, equation (1) can be integrated to give:

$$\frac{[\text{TOC}]}{[\text{TOC}]_0} = e^{-k_1 t} \quad (3)$$

where  $t$  is stripping time in hours and  $[\text{TOC}]$  and  $[\text{TOC}]_0$  are concentrations at time  $t$  and time zero, respectively. Percentage of TOC removal is then:

$$\text{Percent TOC removal} = \left(1 - \frac{[\text{TOC}]}{[\text{TOC}]_0}\right) \times 100\%$$

$$\text{and, percent TOC removal} = (1 - e^{-k_1 t}) \times 100\% \quad (4)$$

Equations (2) and (4) relate mixing and stripping characteristics of a reactor for the laboratory wastewater. Equation (2) was obtained from data generated in the 4-liter fermentor at the University of Illinois. Table 4 shows that calculated TOC and actual TOC removal percentages were in good agreement at moderately high VVM values ( $\geq 0.67$ ). Such good agreement between actual TOC removal experienced at USAMBRDL and calculated TOC removal based on University of Illinois data at comparable  $k_L a$  values indicates that  $k_L a$  is a useful parameter for reactor scale-up and for correlating performance among different reactor configurations while being used as strippers for removing volatile organics.

TABLE 4. COMPARISON OF ACTUAL AND CALCULATED TOC REMOVALS AFTER 1 HOUR BATCH STRIPPING AT VARIOUS GAS/LIQUID RATIOS<sup>35</sup>

VVM	Percent TOC Removal (actual)	Average $k_L a$ , $\text{hr}^{-1}$ (actual)	$k_1$ , $\text{hr}^{-1}$ (calculated) <sup>a</sup>	Percent TOC Removal (calculated) <sup>b</sup>
0.29	2.6	138	0.08	7.7
0.48	6.8	207	0.102	9.7
0.67	9.7	239	0.111	10.6
0.89	11.5	260	0.117	11.1

a. From Equation (2).

b. From Equation (4).

## TREATABILITY STUDIES WITH OZONE AND ULTRAVIOLET LIGHT

A one weight percent ozone concentration was used for the ozone dose. This concentration was considered representative of expected field performance with clean, dried, compressed air as feed to an ozone generator. From the dye dispersion runs, 20 SCFH of air/ozone gas (0.27 VVM) was selected to ensure completely mixed conditions.

Earlier stripping results had indicated that TOC removal via mass transfer of volatile wastewater components from solution was relatively low: 11 percent after 1 hour at 50°C. Nevertheless, it was felt that the effect of this stripping on subsequent ozone oxidation should be explored. The laboratory wastewater is highly refractory towards ozone oxidation even in the presence of ultraviolet light. It was desired to determine if pre-stripping would result in different TOC removal rates due to volatiles being pre-stripped out of solution.

A series of batch oxidation runs was designed in which the synthetic laboratory RO permeate feed was subjected to 0, 1 and 2 hours of continuous pre-stripping. Continuous pre-stripping was done the day before the ozone oxidation runs to ensure that steady state conditions existed at the stripped effluent. Subsequently, the stripped effluent in stage number 1 was batch ozonated at ambient temperature which varied  $23^{\circ} \pm 3^{\circ}\text{C}$  over the series of runs. Table 5 summarizes treatability test experimental conditions.

TABLE 5. EXPERIMENTAL CONDITIONS FOR THE LABORATORY WASTEWATER TREATABILITY STUDIES

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Wastewater:	Synthetic laboratory wastewater after ultra-filtration and reverse osmosis treatment
Pre-stripping:	Temperature: $50^{\circ} \pm 3^{\circ}\text{C}$ Dry air flow: 60 SCFH Volume of stage: $1.2 \text{ ft}^3$ (precontactor) Gas-liquid ratio, VVM = 0.81 Continuous runs: Wastewater flow of 1.2 CFH: 1 hour detention Wastewater flow of 0.6 CFH: 2 hour detention
Ozonation:	Temperature: $23^{\circ} \pm 3^{\circ}\text{C}$ (ambient) Dry air flow: 20 SCFH Volume of stage: $1.2 \text{ ft}^3$ (stage no. 1) Gas-liquid ratio, VVM = 0.27 Ozone concentration in air: 1 weight percent <sup>a</sup> Batch runs (no wastewater flow) Ultraviolet light on

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a. Unless otherwise noted.

Figure 3 shows the effect of pre-stripping on subsequent TOC removal by ozone with ultraviolet light. The polynomial curves plotted are curves of regression estimated by the method of least squares using all data from replicate runs. Curve fitting by this method represented a convenient way to plot the TOC removal trends. For best fit, only first and second degree smooth curves were considered because of the known nature of the TOC removal. Within these constraints curve fitting was good and the proportion of variation explained by regression, R-squared, was 0.97 or higher. For synthetic laboratory wastewater experiencing no pre-stripping, TOC removal was best described by a first degree (linear) expression. The remaining pre-stripping cases were better described by a 2nd degree polynomial expression.

Initial TOC values for each curve reflect the effect of pre-stripping. TOC averaged 130 mg/l for those runs experiencing no pre-stripping. This was less than the theoretical 137 mg/l predicted on the basis of the recipe. It is felt that this is the result of some of the very volatile components like acetone and diethyl ether coming out of solution during recipe makeup (mixing) and before a homogeneous feed sample could be taken and measured. Runs experiencing 1 hour pre-stripping averaged 117 mg/l initial TOC or a 10 percent removal (close to the 11 percent predicted). Those undergoing 2 hour pre-stripping averaged 112 mg/l initial TOC values or 15 percent removal as compared to the no stripping case.

Comparing the 0, 1 and 2 hour pre-stripping TOC removal curves, it is seen that the rate of TOC removal for the no pre-stripping case was slightly greater until about 240 minutes when all the removal rates became approximately the same. Chian had earlier indicated that the TOC removal observed was probably a combination of physical stripping and ozone oxidation, so a series of blank runs were made with ozone and ultraviolet light turned off. In these blank runs the no pre-stripping case experienced a 3 mg/l TOC removal the first hour, then about 1 mg/l/hr thereafter. The pre-stripped wastewaters averaged slightly less than 1 mg/l/hr for the blank runs.

It appears then, that a portion of the initial TOC difference due to pre-stripping in the precontactor was soon made up by stripping in the stages themselves, albeit at undesirable stripping conditions. Figure 3 also shows no high TOC removal rate portion followed by a slower removal rate which was characteristic of the earlier bench scale studies.<sup>9,20</sup> Removal rate remained fairly constant throughout the entire ozonation period.

Figure 4 shows the effect of pre-stripping on subsequent COD removal by ozone with ultraviolet light. The polynomial regression curves were estimated by the method of least squares as previously described. Like Figure 3, initial COD removal was slightly higher for the no pre-stripping case during the first few hours of oxidation. Unlike Figure 3, the rates

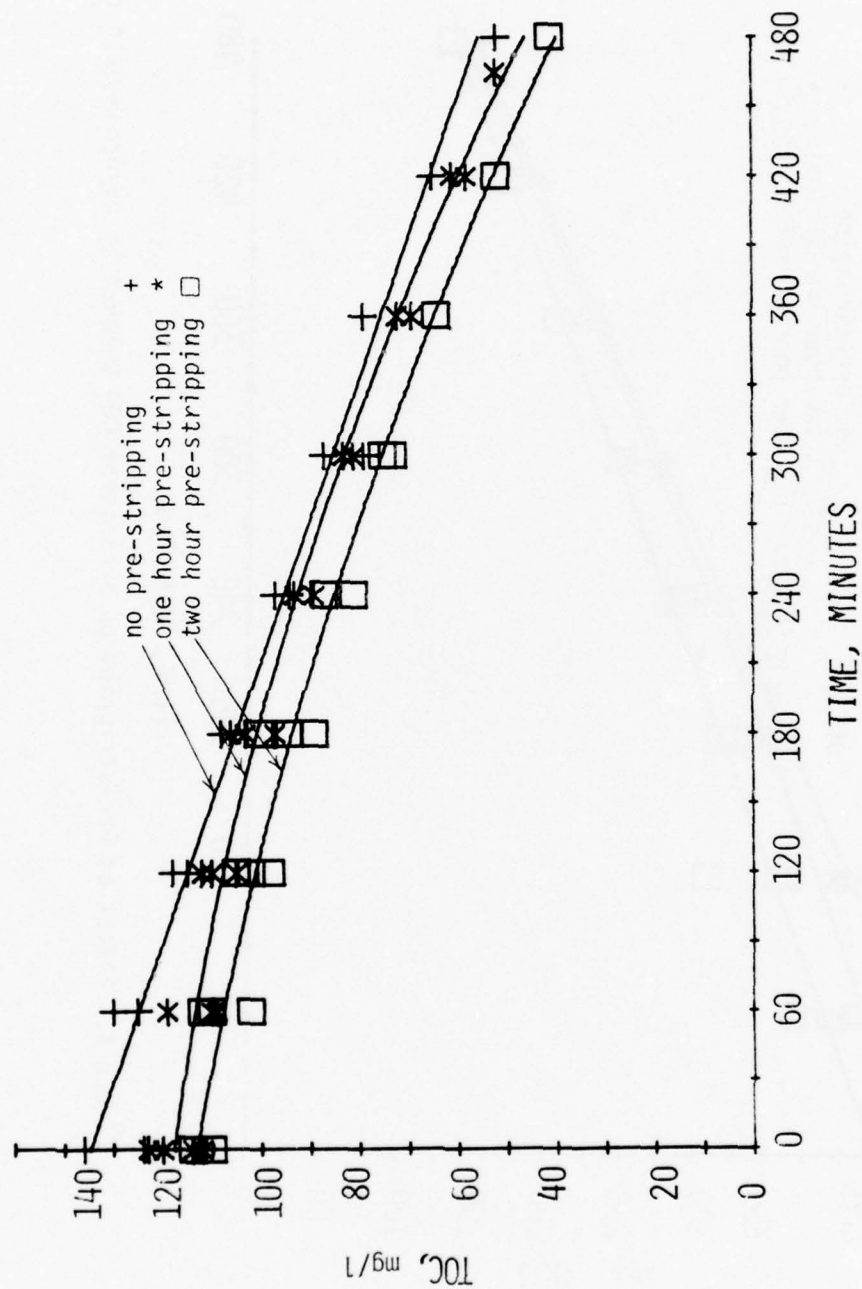


Figure 3. Effect of Pre-stripping on Subsequent TOC Removal by UV/Ozone Oxidation.



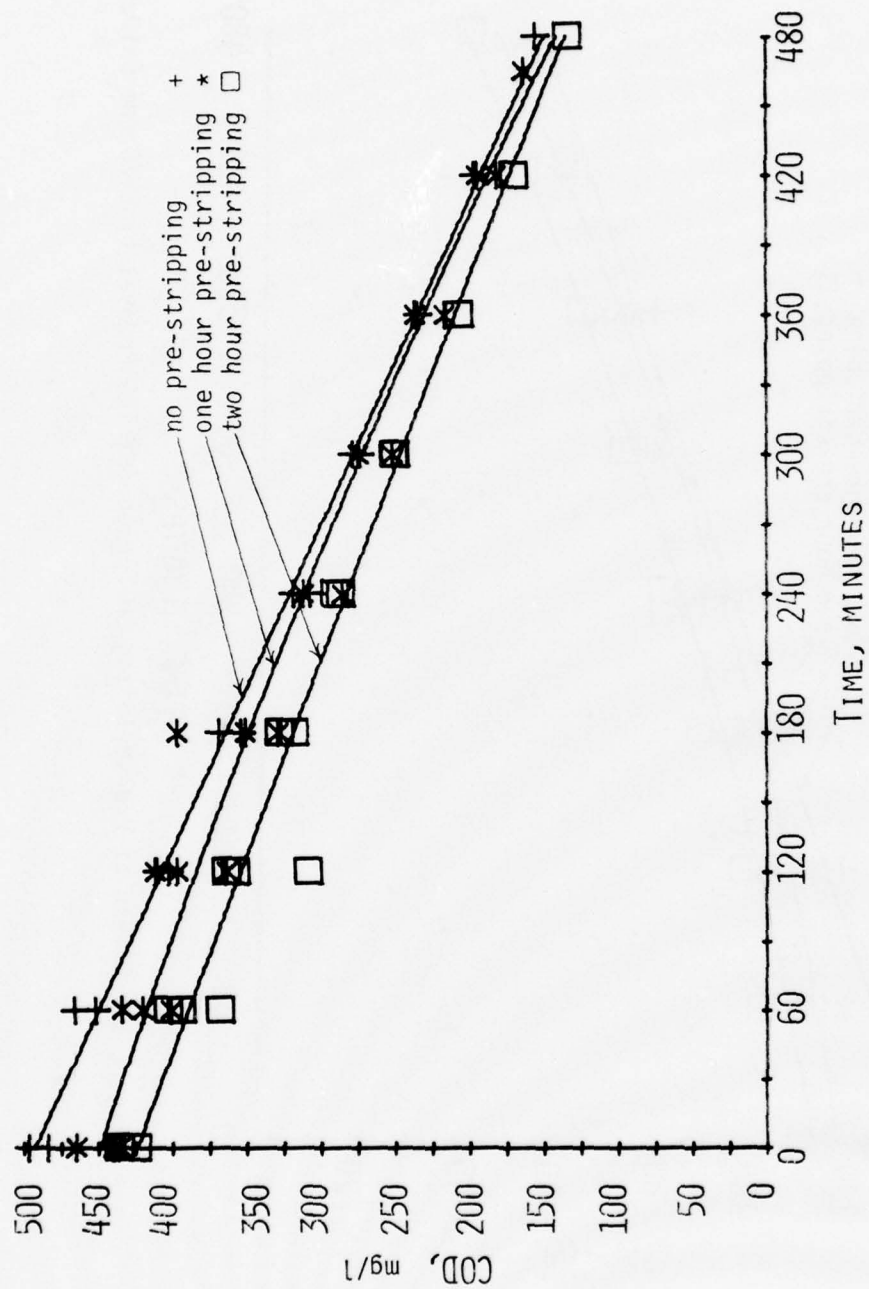


Figure 4. Effect of Pre-stripping on Subsequent COD Removal by UV/Ozone Oxidation.

of COD removal among runs did not appear equal (and parallel) after the first hours of oxidation and appeared to merge. Differences between COD or TOC values among runs after 8 hours were very small and the question became trivial at that point. What was most significant was that COD and TOC removal was very slow and that pre-stripping had lessening importance because of subsequent low conversion.

Methanol and acetone were also measured and are plotted in Figures 5 and 6. The trends reflected those experienced with TOC and COD, which was appropriate since methanol and acetone comprised 79 and 15 percent of the wastewater TOC, respectively. One hour of pre-stripping reduced acetone 30 percent and methanol by about 11 percent. Two hours of pre-stripping reduced acetone and methanol 43 and 18 percent, respectively. After 5 hours of UV/ ozone oxidation, the amount of acetone or methanol remaining was essentially independent of the pre-stripping. The data reflects the previous conclusion that slow conversion essentially negated the benefits derived by pre-stripping before UV/ozonation.

To explore the effect of ozone concentration and ultraviolet light, several runs using 1.5 weight percent ozone in air were made with and without ultraviolet light. They were compared to previous 1 weight percent and 0 weight percent (blank) ozone runs. All runs were made on laboratory wastewater experiencing no pre-stripping. Average results from replicate runs are plotted in Figures 7 through 12.

Comparing Figures 7 and 8 concerning TOC removal, it can be seen that ultraviolet light did improve removal when ozone was present. During the blank runs, no improvement could be seen with or without UV. Increasing the ozone concentration to 1.5 percent and adding UV resulted in a TOC of less than 5 mg/l between 7 and 8 hours. This compares to over 10 hours required for similar conditions and 1 percent ozone gas concentration. These same conclusions can be made for COD data.

Figure 9 shows that no significant amount of methanol was removed during the blank runs whether or not ultraviolet light was present. Significant methanol conversion occurred only when ozone was added to the airflow. Ultraviolet light further enhanced methanol conversion.

Acetone is more easily stripped as shown in Figure 10. This is not surprising considering its boiling point (56.2°C) and that of methanol (64.7°C). Stripping runs were done at 50°C. Figure 10 indicates that acetone responded poorly to ozone oxidation until the ultraviolet light was added. Results from the blank run with UV and the 1.5 percent ozone concentration run without UV were nearly the same. This suggests that ultraviolet light was to some degree affecting the acetone itself. Best results were obtained when 1.5 percent ozone and ultraviolet light were both used.

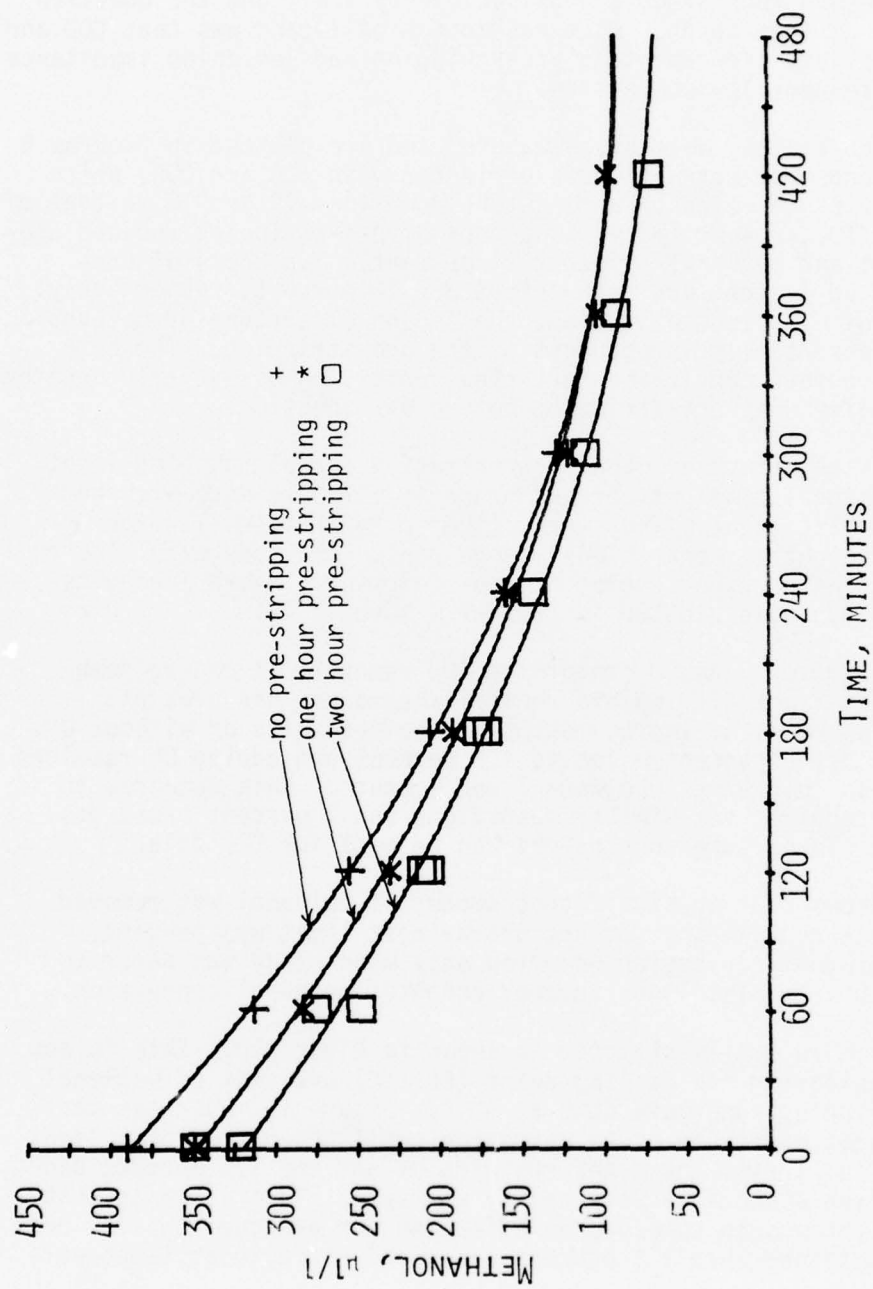


Figure 5. Effect of Pre-stripping on Subsequent Methanol Removal by UV/Ozone Oxidation.

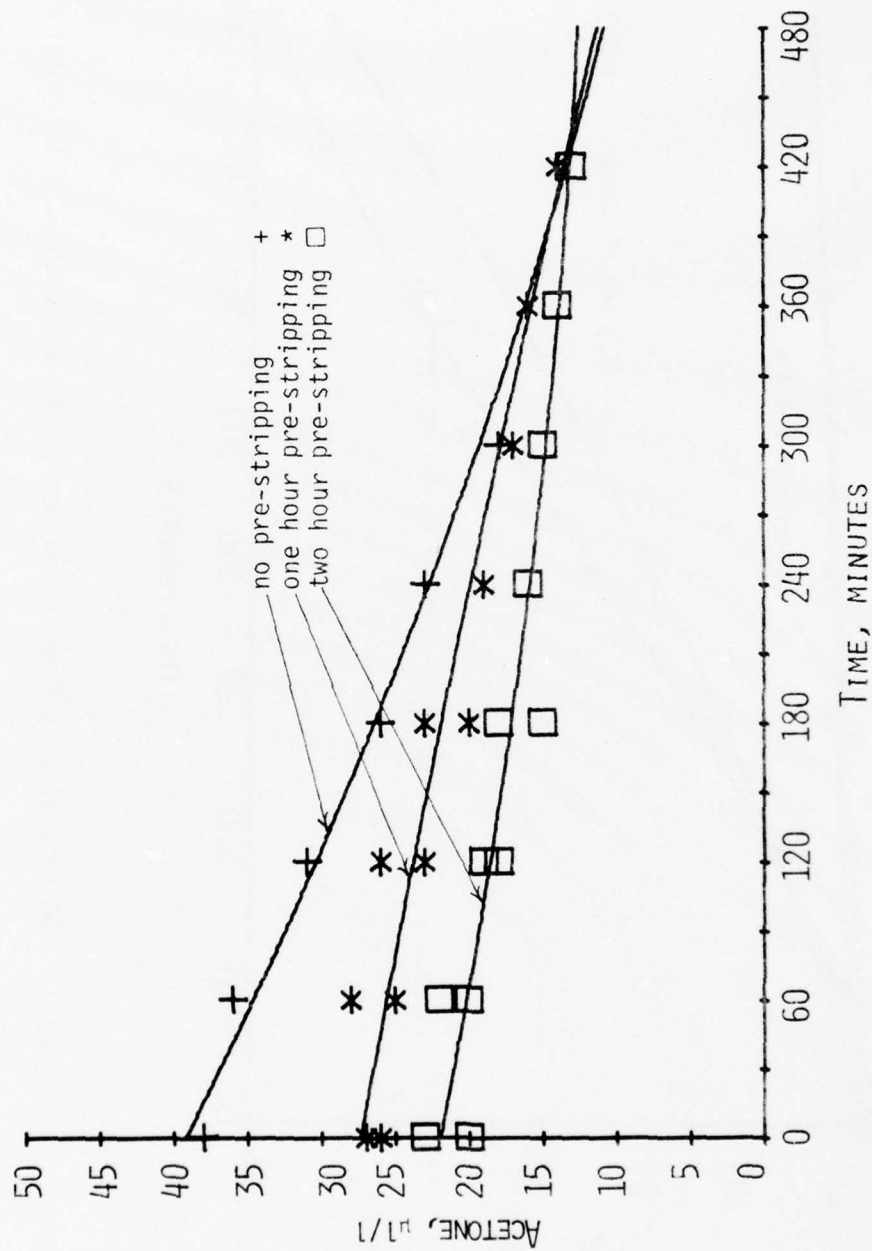


Figure 6. Effect of Pre-stripping on Subsequent Acetone Removal by UV/Ozone Oxidation.



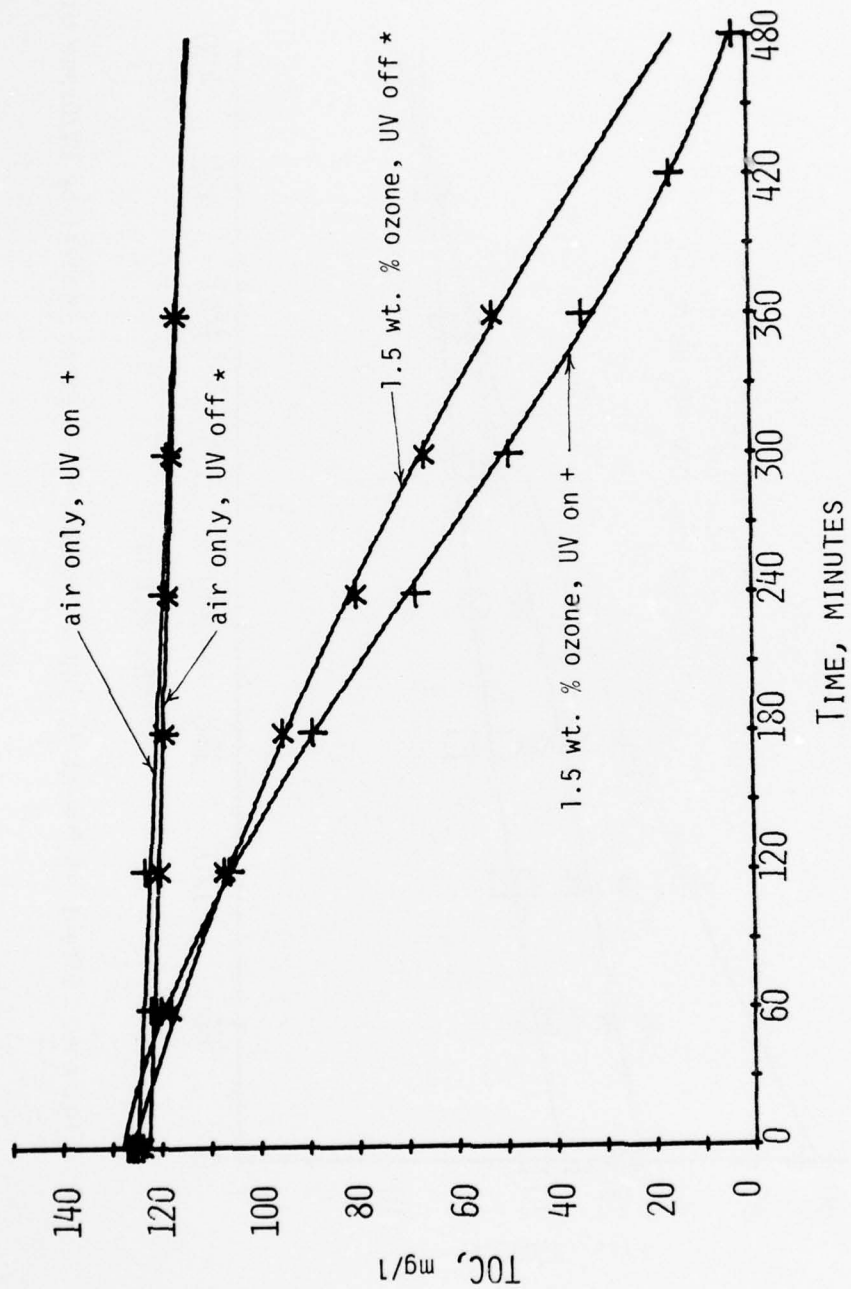


Figure 7. TOC Removal at a Fixed Ozone Dose, With and Without Ultraviolet Light.

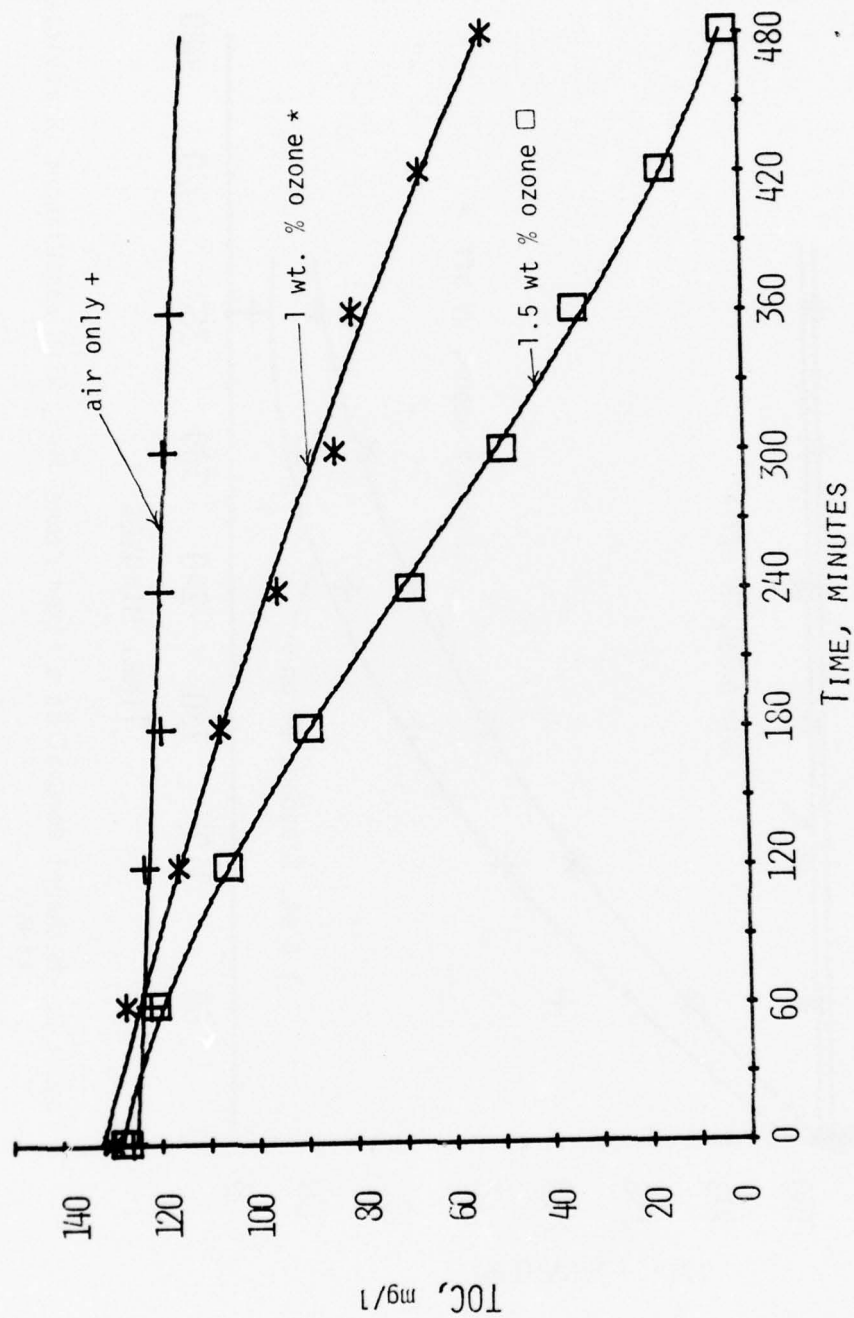


Figure 8. TOC Removal at Various Ozone Doses With Ultraviolet Light.

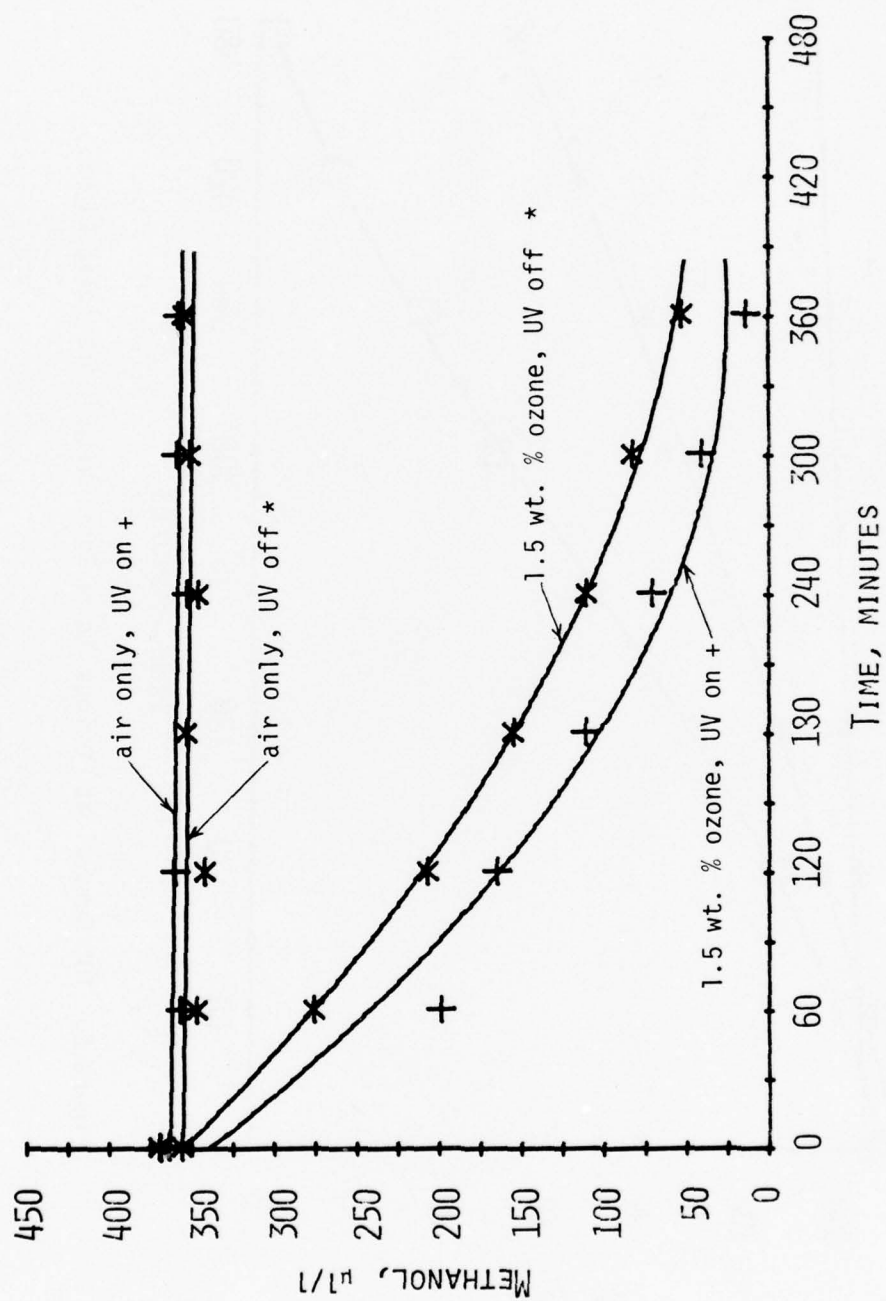


Figure 9. Methanol Removal at a Fixed Ozone Dose, With and Without Ultraviolet Light.

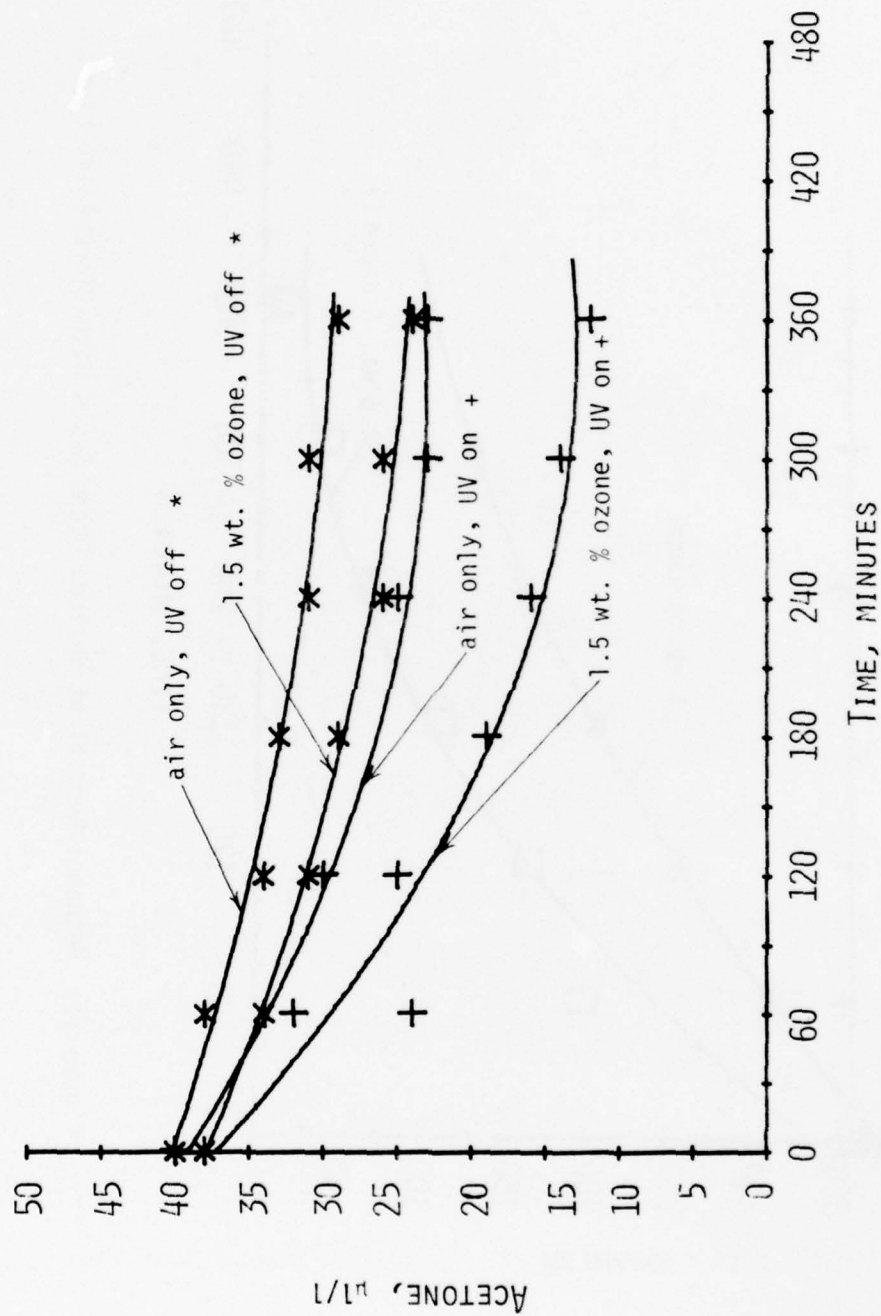


Figure 10. Acetone Removal at a Fixed Ozone Dose, With and Without Ultraviolet Light.

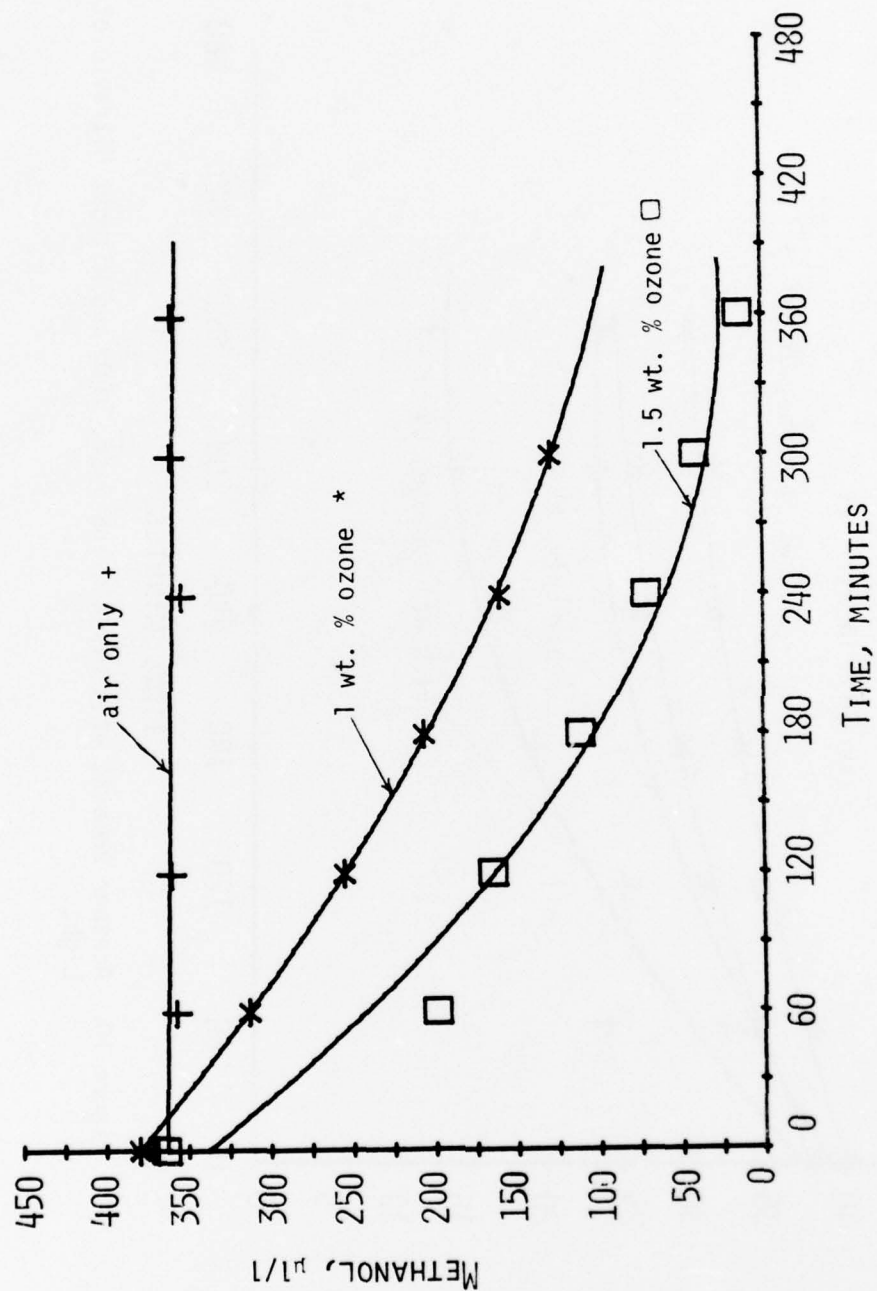


Figure 11. Methanol Removal at Various Ozone Doses With Ultraviolet Light.

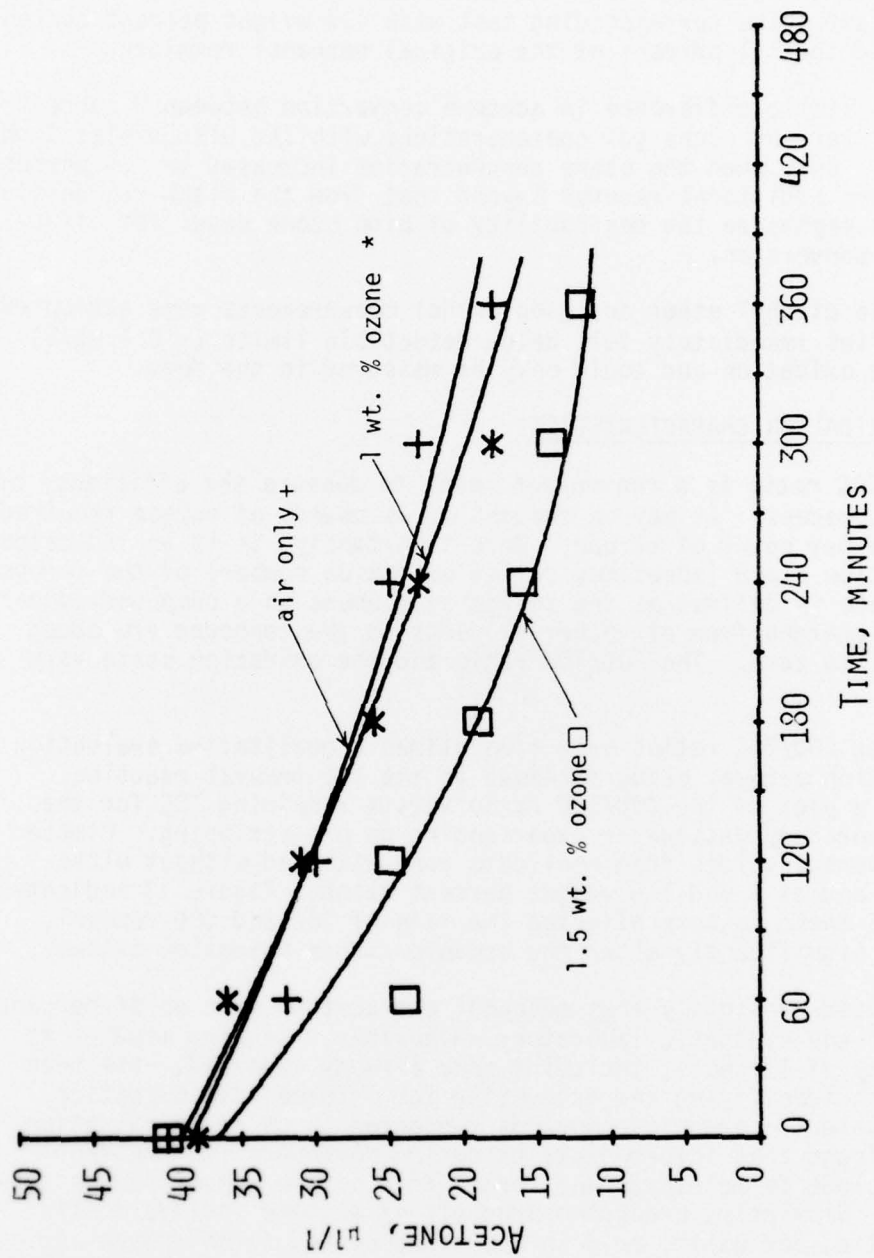


Figure 12. Acetone Removal at Various Ozone Doses With Ultraviolet Light.



Methanol conversion was significantly affected by ozone concentration as shown in Figure 11. After 5 hours, 33 percent of the original methanol content remained in solution when the batch was dosed with 1 percent ozone by weight in air. The corresponding test with 1.5 weight percent concentration showed that 11 percent of the original methanol remained.

There was little difference in acetone conversion between 0 percent (blank) and 1 percent ozone gas concentrations with the ultraviolet light on (Fig. 12). Only when the ozone concentration increased to 1.5 percent did significant additional removal beyond that from the blank run develop. These results emphasize the desirability of high ozone doses for effective acetone conversion.

Comparable diethyl ether and isopropanol measurements were attempted. Their quantities immediately fell below detectable limits ( $< 0.1$  mg/l) upon UV-ozone oxidation and could only be measured in the feed.

#### WASTEWATER OXIDATION CHARACTERISTICS

The COD/TOC ratio is a convenient means to measure the efficiency of an oxidation process. It may be thought of as pounds of oxygen required for oxidation per pound of carbon. More importantly, it is an indicator of the oxidation state (sometimes called oxidation number) of the carbon. Oxidation state is defined as the charge an element in a compound appears to have when charges from all other elements in the compound are added and set equal to zero. The COD/TOC ratio and the oxidation state vary inversely.

Monitoring COD/TOC ratios over time allows a qualitative evaluation of the oxidation pathway being followed in the TOC removal reaction. Figure 13 is a plot of the COD/TOC ratio versus remaining TOC for the synthetic laboratory wastewater experiencing no pre-stripping. Plotted points are average values from replicate runs with and without ultraviolet light and at 1 and 1.5 weight percent ozone. Figure 13 indicates that although these factors affected the rate of TOC and COD removal, they did not significantly alter the organic carbon oxidation pathway.

It was noted previously that methanol and acetone made up 94 percent of the TOC in the synthetic laboratory wastewater. Ongoing studies at the University of Illinois, including some already reported, have been concerned with identifying and accounting for intermediate oxidation products of selected organic compounds subjected to UV/ozone oxidation.<sup>37</sup> It has been found that intermediate oxidation compounds from methanol oxidation include formaldehyde and formic acid before conversion to carbon dioxide. Similarly, breakdown products of acetone include acetic acid, glyoxilic, and oxalic acid in one sequence and formaldehyde and formic acid in another. Table 6 lists these products and their COD/TOC ratios.

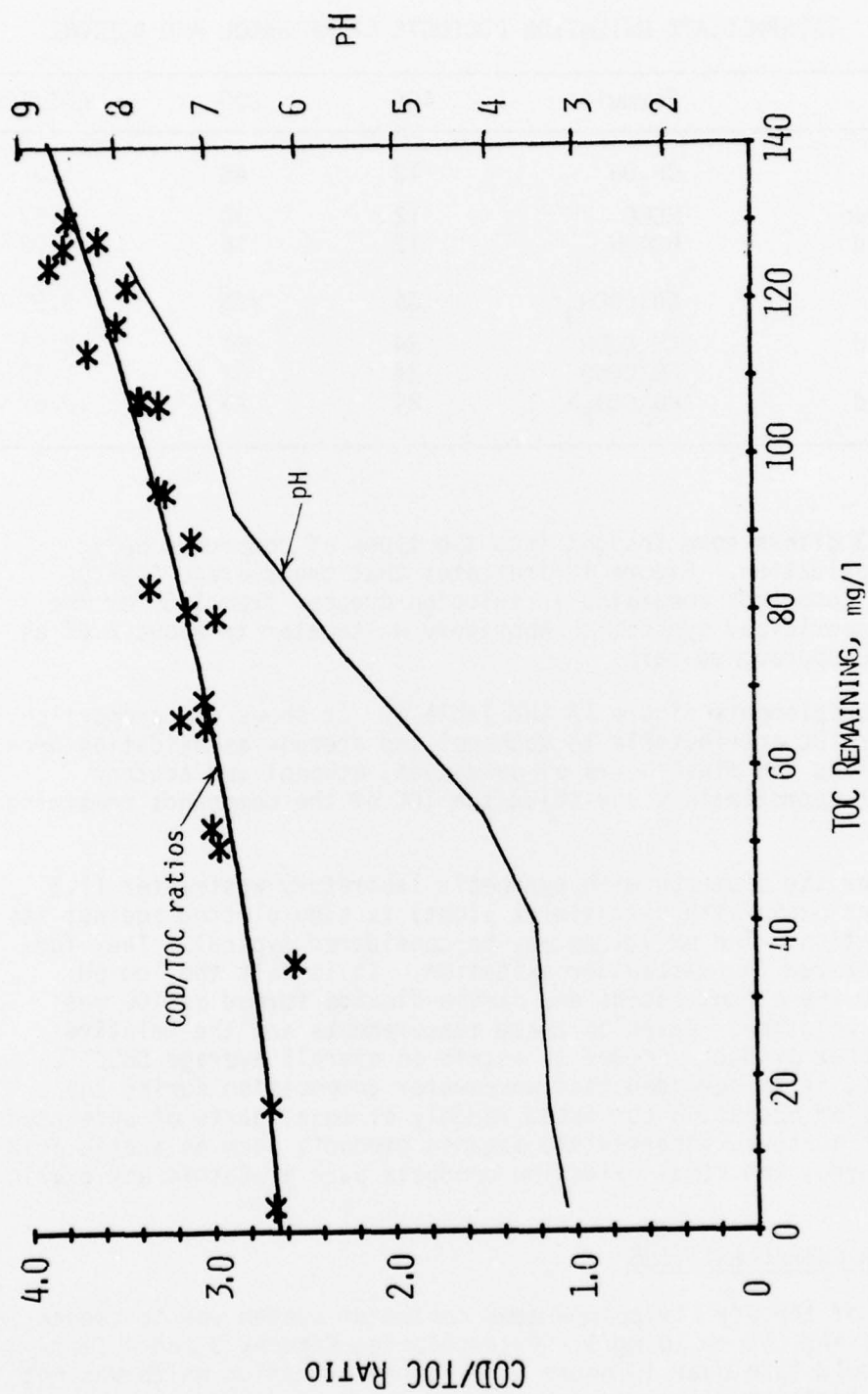


Figure 13. Organic Carbon Oxidation Pathway With Typical pH Changes.



TABLE 6. INTERMEDIATE OXIDATION PRODUCTS OF METHANOL AND ACETONE

Name	Formula	TOC	COD	COD/TOC
Methanol	$\text{CH}_3\text{OH}$	12	48	4.0
Formaldehyde	$\text{HCHO}$	12	32	2.67
Formic acid	$\text{HCOOH}$	12	16	1.33
Acetone	$\text{CH}_3\text{COCH}_3$	36	128	3.55
Acetic acid	$\text{CH}_3\text{COOH}$	24	64	2.66
Glyoxilic	$\text{HO}_2\text{CCHO}$	24	32	1.33
Oxalic acid	$\text{HO}_2\text{CCO}_2\text{H}$	24	16	0.67

Figure 13 offers some insight into the types of compounds being formed upon oxidation. Figure 13 indicates that the average COD/TOC ratio of the compounds remaining in solution dropped from 3.8 for the unstripped, unoxidized synthetic laboratory wastewater to about 2.65 as remaining TOC approached zero.

Table 7 supplements Figure 13 and Table 6. It shows the proportion of wastewater TOC attributable to methanol and acetone as oxidation progressed. During the final hours of oxidation, ethanol and acetone accounted for approximately one-third the TOC of the compounds remaining in solution.

The pH for the best run with synthetic laboratory wastewater (1.5 weight percent ozone with ultraviolet light) is also plotted against its TOC concentration. The pH values may be considered typical. They further characterized the wastewater oxidation. It is felt the low pH resulted from the organic acids and carbon dioxide formed as TOC was removed from solution. Based on these measurements and the relative volumes of other products needed to attain an overall average COD/TOC ratio of 2.65, it is surmised that wastewater composition during the latter stages of ozonation consisted roughly of equal parts of unreacted methanol plus acetone, intermediate organic products such as acetic acid and formaldehyde, and final oxidation products such as formic and oxalic acids.

#### MASS TRANSFER CHARACTERISTICS

The goal of the air stripping-ozone contactor system was to reduce TOC to 5 mg/l and COD to 10 mg/l. Extrapolating Figures 3 and 4 indicated this would take over 10 hours of UV-ozone oxidation which was not acceptable. Additional measurements provided some insight into the limiting factors.

TABLE 7. A COMPARISON OF TOTAL TOC AND THE PORTION CONTRIBUTED BY METHANOL AND ACETONE FOR ONE RUN<sup>a</sup>

Time Into Run (min)	Total Wastewater TOC (mg/l)	TOC Contributed by Methanol	TOC Contributed by Acetone	Contribution from Acetone and Methanol	Percent of Total TOC
0	126	108	20	128	101
60	121	59	12	71	59
120	107	49	12	61	57
180	89	33	9	42	47
240	68	21	8	29	43
300	49	12	7	19	39
360	34	4	6	10	29
420	16	2	3	5	31
480	3	-	-	-	-

a. Run conditions were 1.5 weight percent ozone, UV light on.

Dissolved ozone in water measurements were made in a run using tap water and operating conditions similar to those of the treatability runs. Figure 14 plots the dissolved ozone content versus time during this latter run and lists the conditions of the test. In Figure 14 the dissolved ozone saturation value approaches 3 mg/l which is much higher than the 0.1-0.4 mg/l concentrations experienced earlier with synthetic laboratory wastewater but less than the theoretical solubility of ozone in water of 5.5 mg/l for the test conditions. The difference was probably due to ozone losses in the lines, through the sparger, and during sampling and measurement.

Figure 14 also shows the effect of ultraviolet light on ozone decomposition in aqueous solution. As soon as the ultraviolet light was turned on, dissolved ozone concentration immediately dropped to between 0.1 and 0.4 mg/l and did not increase. Similar observations have been made elsewhere<sup>11</sup> and suggest one possible reason why ultraviolet light used in conjunction with ozone increases the rate of TOC removal when oxidizing refractory compounds. Hewes and Davidson reported that COD removal was roughly proportional to the ozone decomposition products which are probably short-lived free radicals and ions rather than to the concentration of undecomposed ozone itself.<sup>12</sup>

The low dissolved ozone measurements in tap water when the UV light was on raised the question about whether the low ozone concentrations experienced during the laboratory wastewater treatability tests were solely due to UV light decomposition. A blank run using laboratory

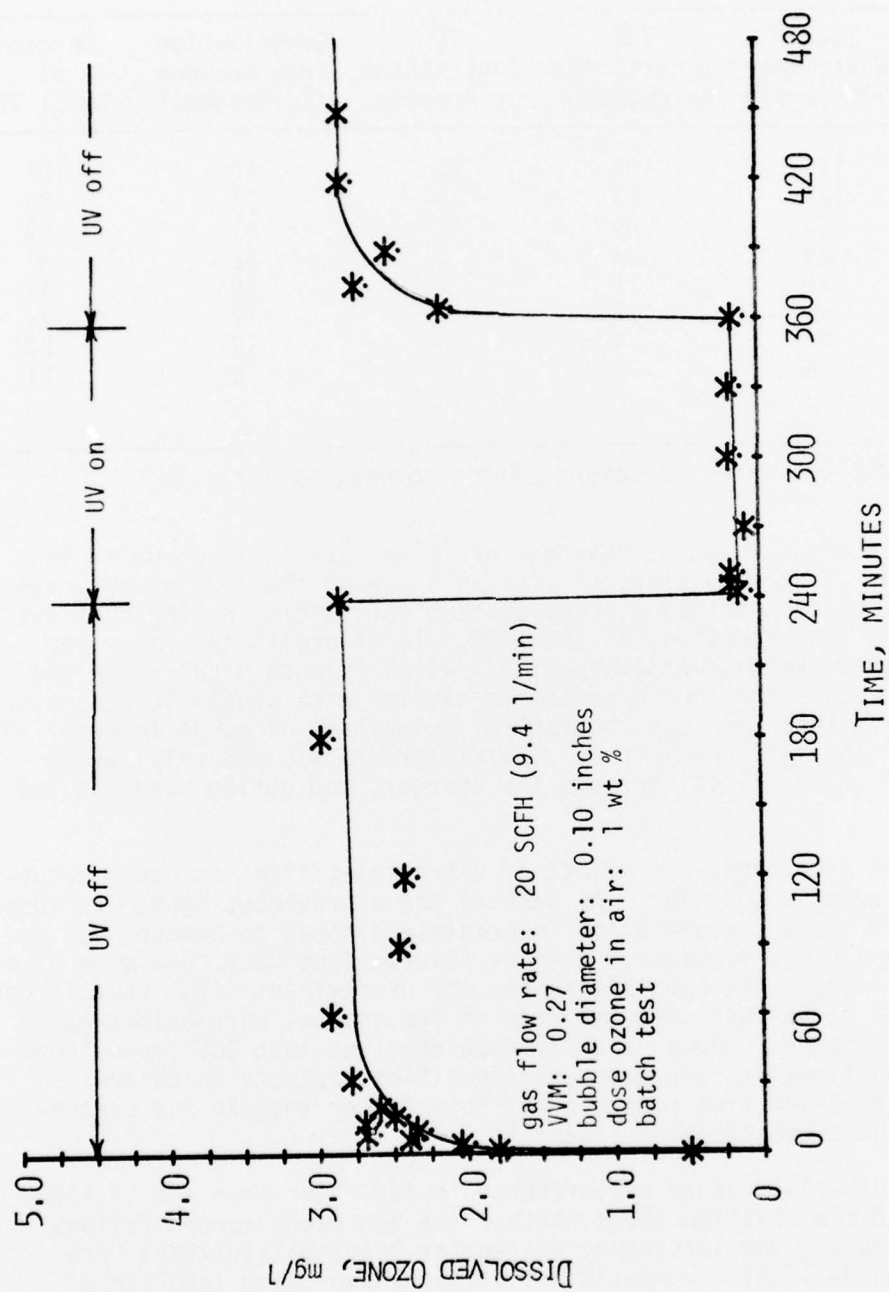


Figure 14. Dissolved Ozone Uptake in Tapwater.

wastewater but with no ultraviolet light was done with laboratory wastewater which had been previously stripped for 2 hours (the "best" wastewater) and dissolved ozone measurements were made. Dissolved ozone ranged from 0.1 to 0.3 mg/l over the 8 hour run. No significance was put on fluctuations within this range as they reflect the precision of the test. It was concluded that mass transfer of ozone into solution was the principal rate limiting factor affecting the treatability tests since dissolved ozone concentration in aqueous solution never approached 3 mg/l and remained between 0.1 and 0.4 milligrams of ozone per liter of wastewater.

It is felt that rate of chemical oxidation of the synthetic laboratory wastewater was influenced by three main factors. First was the concentration of COD or TOC. TOC and COD data were both tested to see if the rate of reaction (chemical oxidation) was of first or second order with respect to their concentration and it was not. The order is probably between zero and one. The former order would be the case if dissolved ozone concentration in the wastewater was zero. The latter order was found by Walden and Life Systems for ozone saturation conditions.<sup>9,20</sup> The second factor was the concentration of the dissolved ozone in the wastewater, which becomes constant at saturation. The third factor was the intensity of the ultraviolet light.

Measurement of the dissolved ozone uptake into the tap water did allow calculation of the overall mass transfer coefficient  $k_L a$  based on the liquid phase fraction. The ozone mass transfer coefficient was found to be  $14.23 \text{ hr}^{-1}$ . During investigation of mass transfer in a sparged reactor, Hill<sup>10</sup> had found the volumetric interfacial area,  $a$ , to be  $11.94 \text{ ft}^{-1}$  for similar operating conditions (gas flow rate of 9.0 l/min, VVM of 0.33 and bubble diameter of 0.125 inches). Using this value for  $a$ , the mass transfer coefficient,  $k_L$ , is 1.19 ft/hr. Multiplying through by the molar liquid density to obtain the ozone transfer flux  $k_x$ , as did Hill,  $k_x$  based on liquid phase driving forces becomes  $4.13 \text{ lb-mole/ft}^2\text{-hr}$ . This compares with  $6.76 \text{ lb-mole/ft}^2\text{-hr}$  Hill measured for the gas-liquid flow conditions noted above but with a 3 weight percent ozone in gas concentration. It also can be compared to the  $7.75 \text{ lb-mole/ft}^2\text{-hr}$  LSI assumed during design of the contactor for a 4.5 l/min gas flow, a 0.10 inch bubble diameter and a 3 percent ozone in gas concentration.



## SUMMARY AND CONCLUSIONS

Longitudinal dye dispersion tests demonstrated that gas flow rates of at least 20 SCFH (0.26 VVM) were necessary to approach hydraulic completely mixed conditions within a contactor stage. Increasing the gas flow rate did not improve mixing. Stripping experiments using different contactors at the University of Illinois and at the U.S. Army Medical Bioengineering Research and Development Laboratory further related stripping and mixing characteristics for a synthetic laboratory RO permeate. A relationship was shown to exist between the stripping rate constant,  $k_1$ , and the corresponding oxygen transfer coefficient,  $k_L a$ , for moderately high gas flow/liquid volume ratios.

Despite good mixing, ozone oxidation with ultraviolet light of the synthetic laboratory wastewater was poor. The relatively low 1 percent weight ozone in air dose was felt to be the major factor. Dissolved ozone measurements in solution were very low (0.1-0.4 mg/l) throughout the treatability tests compared to a demonstrated potential of 3 mg/l. In addition, the measured ozone mass transfer coefficient for the conditions of the experiment was significantly less than that used during design of the contactor. It was concluded that inadequate mass transfer of ozone into solution rather than reaction rate was the principal cause of the slow TOC removal. Such slow removal effectively negated any initial benefit gained from pre-stripping.

Methanol and acetone were the two largest laboratory RO permeate components. Data indicated that the rate of methanol conversion was principally affected by the ozone concentration in the air. The rate of acetone conversion was most affected by the presence or absence of ultraviolet light. The organic carbon oxidation pathway as monitored by COD/TOC ratios was not affected by higher ozone concentration or ultraviolet light. Data indicated that although these factors increased the rate of TOC and COD removal, they did not affect the ratios themselves.



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LIST OF ABBREVIATIONS AND ACRONYMS

a	volumetric interfacial area
C	concentration (at any time t)
°C	degrees Celsius
CFH	cubic feet per hour
C <sub>I</sub>	initial concentration
COD	chemical oxygen demand
ft	feet
gmw	gram molecular weight
gpd	gallons per day
hr	hour
k <sub>1</sub>	first order stripping rate constant
k <sub>L</sub> a	overall mass transfer coefficient, liquid phase basis
k <sub>x</sub>	mass transfer flux, liquid phase basis
l	liter
lb	pound
LMTOC	Life System Modified Torricelli Ozone Contactor
LSI	Life Systems, Inc.
mg/l	milligrams per liter
min	minute
MUST	Medical Unit, Self-Contained, Transportable
nm	nanometers
RO	reverse osmosis
SCFH	standard cubic feet per hour
sec	second
TOC	total organic carbon
UF	ultrafiltration
USAMBRDL	United States Army Medical Bioengineering and Research Laboratory
UV	ultraviolet light
VVM	volume of gas per minute per unit volume of liquid
WPE	Water Processing Element
μl	microliter
μwatts	microwatts



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